92588 Pat. Appl. IN-27 50981

NASA CASE NO. LAR 14538-1

PRINT FIG. 1

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LaRC

(NASA-Case-LAR-14538-1) A PROCESS FOR PREPARING AN ASSEMBLY OF AN ARTICLE AND A POLYIMIDE WHICH RESISTS DIMENSIONAL CHANGE, DELAMINATION, AND DEBONDING WHEN EXPOSED TO CHANGES IN TEMPERATURE Patent Application H1/27

N92-11201

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AWARDS ABSTRACT

A PROCESS FOR PREPARING AN ASSEMBLY OF AN ARTICLE AND A POLYIMIDE WHICH RESISTS DIMENSIONAL CHANGE, DELAMINATION, AND DEBONDING WHEN EXPOSED TO CHANGES IN TEMPERATURE

NASA Case No. LAR 14538-1

Polyimides have higher coefficients of thermal expansion (CTE) than metals, ceramics, and glasses. By lowering the CTEs of polyimides, there is an increase in their usefulness for aerospace and electronic applications where dimensional stability is a requirement. The CTEs of polyimides have been lowered in the past by linearizing the polymer molecular structure or by controlling the orientation of the polyimide film.

By the present invention, an assembly of an article and a low CTE polyimide is prepared. The assembly resists dimensional change, delamination, and debonding when exposed to changes in temperature. A polyamic acid solution was prepared by adding a metal ion-containing additive to the solution. The low CTE polyimide is combined with the article to form the assembly.

The novelty of this invention resides in the preparation of an assembly of an article and a polyimide which resists dimensional change, delamination, or debonding when exposed to temperature changes. This is accomplished by lowering the CTE of the polyimide so it more closely matches that of the article by incorporating a metal ion-containing additive into the polyamic acid solution. The additives which were used with the soluble polyimide could not be used in polyamic acid solutions because they caused the polymer to gel. The use of a polyamic acid solution eliminates the step of having to form the imide and redissolve it prior to use.

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A PROCESS FOR PREPARING AN ASSEMBLY OF AN ARTICLE AND A POLYIMIDE WHICH RESISTS DIMENSIONAL CHANGE, DELAMINATION, AND DEBONDING WHEN EXPOSED TO CHANGES IN TEMPERATURE

Cross Reference to Related Cases:

This application is related to co-pending patent application serial no. ____, filed _____, entitled "A Process for Preparing an Assembly of an Article and a Soluble Polyimide which resists Dimensional Change, Delamination, and Debonding when Exposed to Changes in Temperature".

Origin of the Invention

The invention described herein was made by employees of the United States Government and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefor.

Background of the Invention

1. Field of the Invention

This invention relates to polyimides which have a low coefficient of thermal expansion (CTE). More particularly, it relates to the preparation of an assembly of an article and a polyimide which resists dimensional change, delamination and debonding when exposed to changes in temperature.

2. Description of the Related Art

Polyimides have become widely used as high performance polymers as a result of their excellent thermal stability and toughness. However, polymers in general, including polyimides, have higher CTEs than metals, ceramics, and glasses. Lowering the CTE of polyimides would increase their usefulness for aerospace and electronic applications where dimensional stability is a requirement.

The CTEs of polyimides have been lowered in the past by linearizing the polymer molecular structure or by controlling the orientation of the polyimide film. Numata et al. (Polymer Engineering and Science, 28, (4), 906 (1988)) lowered the CTE by synthesizing a linear polyimide. By employing polyimides prepared from pyromellitic dianhydride (PMDA) or 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA) and aromatic diamines that contain only benzene or pyridine rings in para-positions without flexible linkages, they have synthesized polyimides with CTEs from 20-0.4 ppm/°C. Numata and Miwa (Polymer, 30, (60), 1170 (1989)) found that the CTEs of uniaxially stretched polyimide films with rigid and flexible molecular chains were lower than their non-oriented counterparts.

By the present invention, an assembly of an article and a polyimide with a low CTE is prepared. The assembly resists dimensional change, delamination, and debonding when exposed to changes in temperature. The CTEs have been reduced by incorporating a metal ion-containing additive into a polyamic acid solution. St. Clair et al. (U.S. 4,284,461), Taylor et al. (U.S. 4,311,615) and Stoakley and St. Clair ("Lanthanide-Containing Polyimides" Recent Advances in Polyimide Science and Technology, W.D. Weber and M.R. Gupta, Eds., Society of Plastics Engineers, New York, 1987, pp 471-479) used these additives to alter the adhesive, electrical, and magnetic properties of polyimides.

Accordingly, it is the object of the present invention to prepare an

assembly of an article and a polyimide which resists dimensional change, delamination, and debonding when exposed to temperature changes by forming a low CTE polyamic acid solution which is imidized.

Another object of the invention is to reduce the CTE of the polyimide by incorporating a metal ion-containing additive into the polyamic acid solution so it more closely matches the CTE of the article.

Other objects and advantages of the invention will become apparent to those skilled in the art upon consideration of the accompanying disclosure.

Summary of the Invention

An assembly of an article and a low CTE polyimide film or coating is prepared. The assembly resists dimensional change, delamination or debonding when exposed to changes in temperature. An article is provided. A polyamic acid solution was prepared by reacting equimolar quantities of an aromatic diamine and an aromatic dianhydride in a solvent medium. A metal ion-containing additive was added to the solution. Examples of this additive are: $TbCl_3$, $DyCl_3$, $ErCl_3$, $TmCl_3$, $Al(C_5H_7O_2)_3$, and Er_2S_3. The polyamic acid solution was imidized to yield a low CTE metal ion-containing polyimide film, which is then combined with the article to form the assembly.

The article selected for the assembly is: a solar concentrator, antennae, solar cell arrays, second surface mirrors, precision solar reflectors, electronic circuit boards, or any other item known to those skilled in the art. A precision solar reflector is the preferred article for this application.

A polyamic acid solution was prepared at a concentration of 10-15

weight percent. An equimolar quantity of an aromatic diamine was reacted with an aromatic dianhydride in a solvent medium. A metal ion-containing additive was added to the solution at a concentration of 4-30 weight percent. Erbium chloride gave the most effective results for this application.

A thin-film assembly for a solar reflector is prepared. The metal ion-containing polyamic acid solution is poured onto a glass, metal, or other surface having the shape of the reflector. The resin is spun-cast to a thickness of 0.5 to 5.0 mils and heated to produce a low CTE polyimide film. The film is removed from the surface and combined with a reflecting article and protective topcoat to form the assembly.

An article is either coated with or embedded into the metal ion-containing polyamic acid solution or bonded to the low CTE polyimide substrate. The article is also attached to the polyimide substrate by surface-treatment to form the assembly. In cases where the article is coated with or embedded into the polyamic acid solution, thermal imidization is used to form the polyimide. Thermal imidization was performed by heating the solution to about 100°C - 300°C.

A polyimide substrate is formed either thermally or chemically prior to the attachment of an article. Chemical imidization is performed by reacting the polyamic acid solution with acetic anhydride and pyridine, recovering the precipitate, and heating under pressure to fuse the imide powder. The article is bonded to the polyimide substrate with a polyimide-based adhesive or by surface treatment.

Brief Description of the Drawings

Figure 1 is a schematic showing a preferred embodiment of the present invention where the low CTE polyimide is used as a substrate.

Figure 2 is a schematic showing an article which is coated with a low CTE polyimide to form an assembly.

Figure 3 is a schematic showing the formation of an assembly by embedding an article into the low CTE polyimide.

Figure 4 is a schematic showing an article attached to a low CTE polyimide substrate with an adhesive.

Description of the Preferred Embodiments

A solution of a metal ion-containing polyamic acid resin, which yielded a polyimide having a low coefficient of thermal expansion (CTE), was prepared at 10-15% solids. An equimolar quantity of 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) or 2,2-bis(3,4-dicarboxy-phenyl)hexafluoropropane dianhydride (6FDA) was added to a stirred solution of 4,4'-oxydianiline (4,4'-ODA) or 1,3-bis(aminophenoxy)benzene (APB) in a polar organic solvent such as N,N-dimethylacetamide (DMAc). The resulting polyamic acid solution was stirred at room temperature for approximately 2-1/2 hours. A metal ion-containing additive was added at a concentration range of

approximately 4-30 weight percent either before the addition of the monomers, immediately following the addition of the dianhydride or after the polyamic acid polymerization was completed.

The metal ion-containing polyamic acid solution was cast as a film on soda-lime glass plates using a doctor blade set to obtain a cured film thickness of approximately 0.025 mm (1 mil). The film was placed in a low humidity box overnight and then imidized by heating in a forced air oven for 1 hour each at 100°, 200°, and 300°C. The film was removed from the glass plate by soaking in water.

Although the dianhydrides, BTDA and 6FDA, and the diamines, 4,4'-ODA and APB, were used in the polyamic acid polymerization, other dianhydrides and diamines employed in the preparation of polyamic acids or polyimides may be used in the present invention.

The solvent medium for the polyamic acid was DMAc. However, other solvents known to those skilled in the art such as: N,N-dimethylformamide, 1-methyl-2-pyrrolidinone, and dimethyl sulfoxide may be used in the preparation of polyamic acids.

The metal ion-containing additives of this invention included the chlorides of the following lanthanides: terbium ($TbCl_3$), dysprosium ($DyCl_3$), erbium ($ErCl_3$), holmium ($HoCl_3$), and thulium ($TmCl_3$). An additional lanthanide-containing additive used was erbium sulfide (Er_2S_3). One other metal ion-containing additive used was aluminum acetylacetonate ($Al(C_5H_7O_2)_3$). Each additive reduced the CTE and it was found that $ErCl_3$ gave the best results.

The data is shown in Tables I and II.

Table I. Coefficients of Thermal Expansion

of Metal Ion-Containing BTDA/4,4'-ODA Films

Additive	% Additive	Tg by TMA, °C	CTE ppm/°C
BTDA/4,4'-ODA Control	0.0	281	39.1
$TbCl_3$	11.3	297	27.4
$DyCl_3$	11.4	292	26.3
$ErCl_3$	11.6	302	17.0
$TmCl_3$	11.6	314	19.5
Er_2S_3	17.1	303	24.5
$Al(C_5H_7O_2)_3$	11.1	295	27.8

Table II. Coefficients of Thermal Expansion

of Metal Ion-Containing 6FDA/APB Films

Additive	% Additive	CTE, ppm/°C
6FDA/APB Control	0.0	51.0
$TmCl_3$	6.9	35.7
$HoCl_3$	6.8	42.5
$Al(C_5H_7O_2)_3$	8.0	43.3

It was also found that increasing the concentration of the metal ion-containing additive resulted in a decrease in the CTE. Table III gives these results.

Table III. Effect of $TbCl_3$ Concentration on Coefficient of Thermal Expansion

Additive mole Tb^{+3}: mole polymer	% Additive	Coefficient of Thermal Expansion ppm/°C
BTDA/4,4'-ODA Control	0.0	39.1
1:10	4.5	33.3
1:4	11.3	27.4
1:2	22.6	21.0

There were many additional metal ion-containing additives that were found not to be useful for this application. These additives were: holmium acetate, erbium N-phenylphthalamate, erbium acetylacetonate, tin chloride, terbium fluoride, dysprosium fluoride, lutetium fluoride, silver nitrate, gadolinium acetate, holmium sulfide, erbium acetate, cerium acetylacetonate, neodymium acetylacetonate, samarium acetylacetonate, terbium acetylacetonate, praseodymium nitrate, neodymium nitrate, samarium nitrate, holmium nitrate,

erbium nitrate, thulium nitrate, ytterbium nitrate, europium chloride, gadolinium sulfide, terbium sulfide, dysprosium sulfide, terbium iodide, thuluim iodide, and dysprosium bromide. Some of these additives caused the polyamic acid solution to gel while others, although they made good films, were not effective in lowering the CTE. It is for this reason that the additives listed in Tables I and II gave unexpected results.

A low CTE polyimide substrate is prepared by pouring the metal ion-containing polyamic acid solution into a mold, drying then imidizing by heating for one hour each at 100°, 200°, and 300°C. Another method of forming the substrate is to slowly add the metal ion-containing polyamic acid solution to a stirred mixture of acetic anhydride and pyridine. The imide precipitate is recovered, washed with water, and dried. The imide powder is poured into a mold and fused by heating under pressure to form the polyimide substrate.

An article is provided to form an assembly with the polyimide. Examples of this article are: a solar concentrator, antennae, solar cell arrays, second surface mirrors, precision solar reflectors, or electronic circuit boards. Other articles known to those skilled in the art can also be used. A metal ion-containing polyamic acid solution was prepared. The solution is used to coat the article, to embed the article, or to form a substrate to which the article is bonded. For example, a circuit board is coated by either spraying, dipping, or brushing with the polyamic acid solution. The solution is imidized by heating for 1 hour each at 100°, 200°, and 300°C in a forced air oven. The coated article is resistant to delamination when exposed to temperature changes.

In another example, the polyamic acid solution is cast into a mold. The circuit board is embedded into the solution prior to imidizing. After imidizing, the resulting assembly is resistant to debonding.

As another example, an article is attached to a polyimide substrate formed from the polyamic acid solution. The solution is imidized by heating and the article is attached to the substrate with a polyimide-based adhesive. The resulting assembly is resistant to dimensional change, debonding, and delamination when exposed to changes in temperature.

In yet another example, an assembly for a solar reflector is prepared. The metal ion-containing polyamic acid solution is poured onto a glass, metal, or other surface having the shape of the reflector. The resin is spun-cast to a thickness of 0.5 to 5.0 mils and heated to produce a low CTE polyimide film. The film is removed from the surface and combined with a reflecting article and protective topcoat to form the assembly.

EXAMPLES

Example 1

Preparation of the 15% solids polyamic acid solution of BTDA/4,4'-ODA was conducted at room temperature by dissolving 60.07g (0.30 mole) of 4,4'-ODA in 948 ml DMAc. After the diamine was dissolved, 96.67g (0.30 mole) BTDA were added and stirred. After three hours, the polyamic acid solution

was clear yellow with an inherent viscosity of 1.49 dl/g when measured at 0.5% solids in DMAc at 35°C. A film of this control resin was cast on a glass plate at a 15 mil blade gap and left in a low humidity film box overnight. This tack free film was then cured by heating in a forced air oven for one hour each at 100°, 200°, and 300°C. The resulting film had a glass transition temperature of 281°C. The CTE of this yellow control film was determined to be 39.1 ppm/°C over the temperature range of 70-110°C.

To 10.45g of the 15% solids BTDA/4,4'-ODA stock resin was added 0.199g (0.00075 moles) $TbCl_3$ in 2ml DMAc. This mixture was stirred at room temperature for several hours, resulting in a milky white resin. A film of this 1:4 $TbCl_3$:BTDA/4,4'-ODA resin was cast on a glass plate using a 15 mil blade gap. It was placed in a low humidity film box overnight and cured like the control film. The resulting hazy yellow film had a Tg of 297°C and a CTE of 27.4 ppm/°C.

Example 2

The process of Example 1 was repeated using 0.202g (0.00075 moles) $DyCl_3$. The resulting 1:4 $DyCl_3$:BTDA/4,4'-ODA film was a hazy amber film with a Tg of 292°C and a CTE of 26.3 ppm/°C.

Example 3

The process of Example 1 was repeated using 0.205g (0.00075 moles)

$ErCl_3$. The resulting 1:4 $ErCl_3$:BTDA/4,4'-ODA film was a hazy amber film with a Tg of 302°C and CTE of 17.0 ppm/°C.

Example 4

The process of Example 1 was repeated using 0.206g (0.00075 moles) $TmCl_3$. The resulting 1:4 $TmCl_3$:BTDA/4,4'-ODA film was a hazy yellow film with a Tg of 314°C and CTE of 19.5 ppm/°C.

Example 5

The process of Example 1 was repeated using 0.080g (0.0003 moles) $TbCl_3$. The resulting 1:10 $TbCl_3$:BTDA/4,4'-ODA film was a slightly hazy yellow film with a CTE of 33.3 ppm/°C.

Example 6

The process of Example 1 was repeated using 0.398g (0.0015 moles) $TbCl_3$. The resulting 1:2 $TbCl_3$:BTDA/4,4'-ODA film was a hazy amber film with a CTE of 21.0 ppm/°C.

Example 7

The process of Example 1 was repeated using 0.195g (0.0006 moles) $Al(C_5H_7O_2)_3$. The resulting 1:5 $Al(C_5H_7O_2)_3$:BTDA/4,4'-ODA film was a transparent amber film with a coefficient of thermal expansion of 27.8 ppm/°C.

Example 8

To 37.9830g of DMAc, 0.5010g (0.00182 moles) $TmCl_3$ were added. The mixture was stirred at room temperature for approximately 1/2 hour, then 2.6603g (0.0091 moles) APB were added. Stirring was continued until the diamine was dissolved. After dissolution of the diamine, 4.0830g (0.009191 moles) 6FDA were added and stirring was continued for approximately 19 hours.

A film of this resin was cast at 18 mils thickness on a glass plate and placed in a low humidity film box overnight. The resin was cured by heating in a forced air oven for one hour each at 100°, 200°, and 300°C. The resulting peach colored 1:5 $TbCl_3$:6FDA/APB film had a CTE of 35.7 ppm/°C as compared to 51.0 ppm/°C for the colorless control 6FDA/APB film.

Example 9

An article **15** (of Figure 3) is attached to a low CTE polyimide substrate

prepared from the metal ion-containing polyamic acid solution as in Example 1. The solution is poured into a mold and the article is embedded in the solution **16** (of Figure 3). The assembly is imidized by heating for 1 hour each at 100°C, 200°C, and 300°C in a forced air oven. The article is resistant to debonding when exposed to changes in temperature.

Example 10

An article **15** (of Figure 4) is attached to a low CTE polyimide substrate **10** (of Figure 4) prepared from the metal ion-containing polyamic acid solution as in Example 1. The solution is poured into a mold and is imidized by heating for 1 hour each at 100°C, 200°C, and 300°C in a forced air oven. The article is attached to the substrate by bonding it with an adhesive **17** (of Figure 4). The article is resistant to debonding when exposed to changes in temperature.

Example 11

A circuit board **13** (of Figure 2) is coated with a metal ion-containing polyamic acid solution **14** (of Figure 2) as in Example 1. The coating is applied to the circuit board by spraying, brushing, dipping, or any other method known to those skilled in the art. The coating is imidized by heating for 1 hour each at 100°C, 200°C, and 300°C in a forced air oven. The coated article **14** (of Figure 2) is resistant to delamination when exposed to changes in temperature.

Example 12

A thin-film assembly for a solar reflector (Figure 1) is prepared. A metal ion-containing polyamic acid solution as in Example 1 was prepared. The solution is poured onto a glass, metal, or other surface which has the shape of the reflector. The solution is spun-cast to a thickness of 0.5 to 5.0 mils and heated to 100° to 300°C in a forced air oven. The resulting substrate **10** (of Figure 1) is removed from the surface and is metallized with a highly reflecting metal layer **11** (of Figure 1) such as silver, aluminum, or chromium. The metal layer is applied at a thickness between 10 and 2000 Å using a surface treatment such as vapor deposition or sputtering. A clear protective topcoat **12** (of Figure 1) is applied at 0.1 to 1.0 mil thickness to prevent tarnishing. The layers of the assembly are resistant to dimensional change, debonding, or delamination upon exposure to changes in temperature.

The above examples are considered to be illustrative of the invention and there may be modifications and variations in the metal ion-containing additive, the polyimide, or the article that will be apparent to those skilled in the art without departing from the spirit and scope of the invention as set forth herein. It is therefore to be understood that the invention may be practiced otherwise than as specifically described and claimed herein.

What is claimed to be new and desired to be secured by Letters Patent of the United States is:

A PROCESS FOR PREPARING AN ASSEMBLY OF AN ARTICLE AND A POLYIMIDE WHICH RESISTS DIMENSIONAL CHANGE, DELAMINATION, AND DEBONDING WHEN EXPOSED TO CHANGES IN TEMPERATURE

Abstract of the Disclosure

An assembly of an article and a polyimide composition is prepared. The assembly resists dimensional change, delamination, or debonding when exposed to changes in temperature. An article is provided. A polyamic acid solution which yields a polyimide having a low coefficient of thermal expansion (CTE) was prepared. Equimolar quantities of an aromatic diamine and an aromatic dianhydride were reacted in a solvent medium to form a polyamic acid solution. A metal ion-containing additive was added to the solution. Examples of this additive are: $TbCl_3$, $DyCl_3$, $ErCl_3$, $TmCl_3$, $Al(C_5H_7O_2)_3$, and Er_2S_3. The polyamic acid solution was imidized and is combined with the article to form the assembly.

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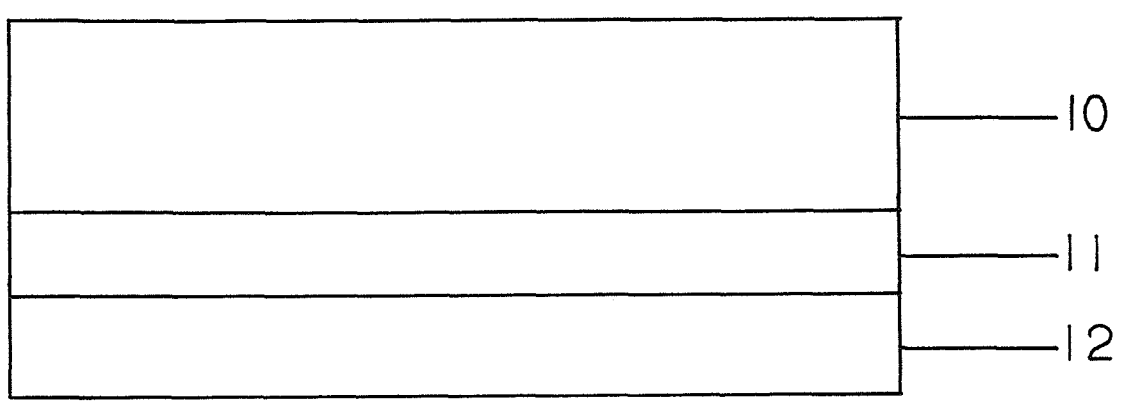

FIGURE 1

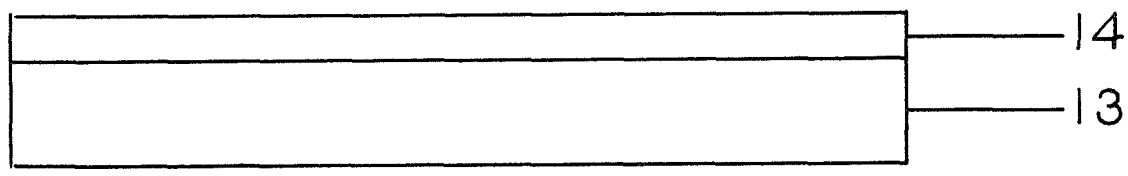

FIGURE 2

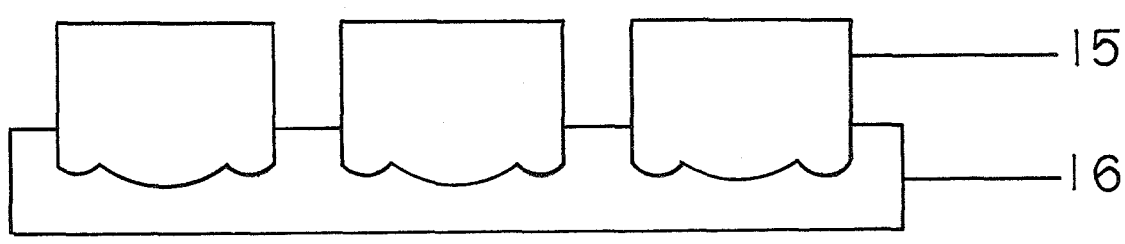

FIGURE 3

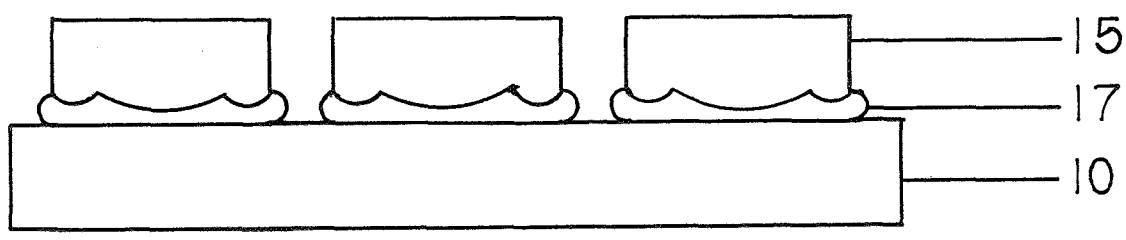

FIGURE 4